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H. J. Kreuzer

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Department of Physics, Dalhousie University
Halifax, Nova Scotia, Canada B3H 3J5

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PHYSICS AND CHEMISTRY IN HIGH ELECTRIC FIELDS

H.J. Kreuzer
Department of Physics, Dalhousie University
Halifax, N.S. B3H 3J5 Canada

ABSTRACT. Progress is reviewed in our understanding of the effects of high electrostatic fields (of the order of volts per angstrom) on the adsorption and reaction of atoms and molecules on metal and semiconductor surfaces.

1. Introduction

Electrostatic fields of the order of volts per angstrom, as they occur over macroscopic distances at field emission tips, in zeolite cavities and at the electrode-electrolyte interface, are of the same order as the fields inside atoms and molecules. They are thus strong enough to induce *re*-arrangement of electronic orbitals of atoms and molecules, in particular at metal surfaces, leading to new phenomena that can be summarily described as field-induced chemisorption and field-induced chemistry. Several review articles have been written in recent years about these topics [1-4].

Electric field effects on matter can be classified, rather arbitrarily, into two categories: (i) in low fields, i.e. below roughly 10^{-1} V/Å, atoms, molecules and condensed matter only get polarized; we will call such effects physical. (ii) In fields larger than typically 10^{-1} V/Å chemical effects come into play in addition in that the electronic orbitals get distorted to such a degree as to effect the chemical characteristics of an atom or molecule e.g. by establishing new bonding orbitals. In this way, molecules, unstable in field free situations, may be stabilized by a strong electric field. Also, new pathways in chemical reactions, e.g. in heterogeneous catalysis and in chemical vapor deposition, may be established.

To discuss field effects qualitatively, we look, in Fig. 1, at a molecule AB adsorbed on a metal. Far from the surface and in the absence of a field, the atomic orbitals of A and B hybridize into molecular orbitals which we take to be a lower-lying bonding orbital and an empty antibonding orbital. As the molecule approaches a metal surface, additional hybridization with the conduction electrons occurs leading to shifts and broadening of these orbitals. As illustrated in Fig. 1, the antibonding orbital gets partially occupied resulting in (i) bonding to the surface and (ii) weakening of

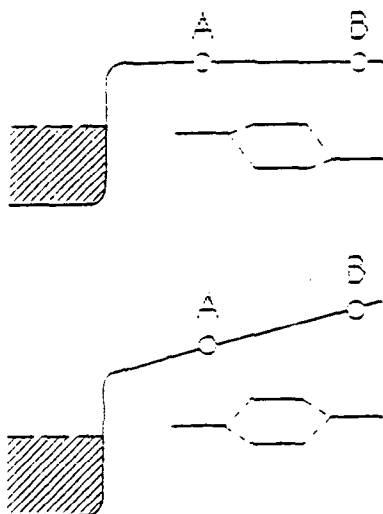


Fig.1: Schematic view of the electronic level structure of an AB molecule adsorbed on a metal without and with an external electric field.

the A-B bond and stretch vibration. Molecules such as CO and N_2 are examples. Applying an electric field, F_0 , pointing away the surface, adds the potential energy, eF_0z , for the electrons outside the metal (assuming, for this simplified discussion, total expulsion of the field from the metal). This raises the atomic levels of the atoms A and B by amounts of the order eF_0z_a and eF_0z_b , respectively, resulting in a substantial *re*-arrangement of the molecular orbitals. For the situation depicted in Fig. 1, the anti-bonding orbital empties out again, leading to restabilization of the molecule and probably a weakening of the surface bond. If we increase the field strength to the point where the bonding orbital is lifted above the Fermi energy of the metal, it will drain as well, leading to field-induced dissociation. Note that in the absence of the field the bonding orbital of the AB molecule is more B-like whereas the anti-bonding orbital has more A character. As the electric field is increased, these characteristics are changed in a continuous manner into a situation where the bonding orbital is more A-like and the anti-bonding orbital has B character. This possibility of changing the relative position of orbitals of the constituent atoms in a molecule with respect to each other, leads to new, field-induced chemistry. As an example, local electric fields, generated by a sharp metal tip, can be used to preferentially dissociate certain species that one wants to deposit locally under the tip, e.g. in field-assisted chemical vapor deposition.

In this paper we will first review our present understanding of electrostatic fields at metal surfaces. Then we will look at field evaporation and field-induced chemisorption. Finally we will discuss in some detail field-induced chemical reactions at surfaces as

the topic of most relevance to atomic and nanoscale manipulation of materials.

2. Electrostatic Fields at Metal Surfaces

Classical electromagnetic theory assumes that the surface of a metal is a mathematical plane with excess charges and a dipole layer at which the normal component of the electric field drops discontinuously to zero, at least for a perfect conductor. On real surfaces, however, the electron distribution and also electric fields vary smoothly over distances of a few angstroms. A simple model [5-7] that bears out these features is the jellium model of a metal in which we assume that the ionic lattice can be smoothed into a uniform positive charge density n_+ that drops to zero abruptly half a lattice constant above the topmost lattice plane. Within the framework of density functional theory, the electron density and the local field distribution can be determined from the selfconsistent solution of a Schrödinger-like equation and of Pois-

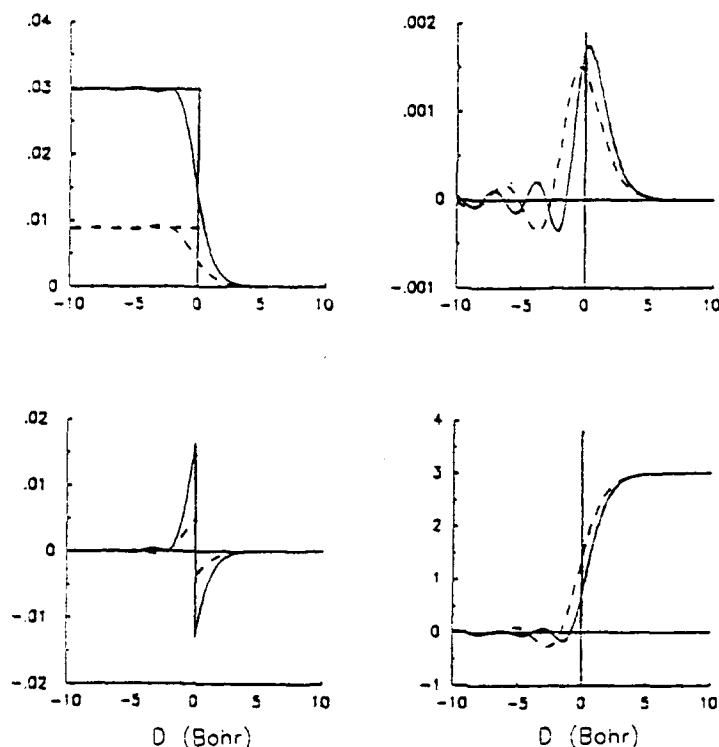


Fig.2: A schematic view of (a) the charge distribution at a metal surface without a field ($F_0=0$), the positive jellium background is indicated, solid lines: $r_s=2.0$, dashed lines: $r_s=3.0$; (b) the surface dipole layer $\rho^s=n_+^s-n_-^s$ for $F_0=0$, constructed from (a); (c) the field-induced surface charge $\delta\rho$; and (d) the applied electric field F at a metal surface.

son's equation. In Fig.2 we present the results of a density functional calculation for a jellium surface. In panel (a) we show the selfconsistent electron distribution in the absence of an external field with the local deviation from charge neutrality, i.e. the dipole layer, given in panel (b). In panel (c) we have added some excess charge, $\delta\rho$, that gives rise to the external field in panel (d). We note that the field decays smoothly into the metal with appreciable strength left at the position of the top most ion layer. This can be viewed as partial penetration of the field into the metal, or as incomplete expulsion of the field from the metal. To compare these quantum mechanical calculations with classical results from Maxwell's theory, we note that the plane at which boundary conditions are imposed on the classical fields, i.e. the discontinuous drop of the normal component of the electric field to zero, is given by the center of gravity of the excess charge $\delta\rho$, i.e. roughly the point where the field has dropped to half its value at infinity. For future reference we note here that this plane does not remain constant but moves towards the ion cores as the asymptotic field strength increases, due to the fact that the electrons are pushed into the metal increasing the field penetration and the Friedel oscillations.

Density functional calculations have recently been performed to deal with the situation with a lonely metal atom on a flat, close-packed metal surface.[8] The latter was modeled by a flat jellium surface with the metal atom treated ab initio. The calculations are based on the chemisorption programme of Lang and Williams [9], extended to account for the external field selfconsistently as

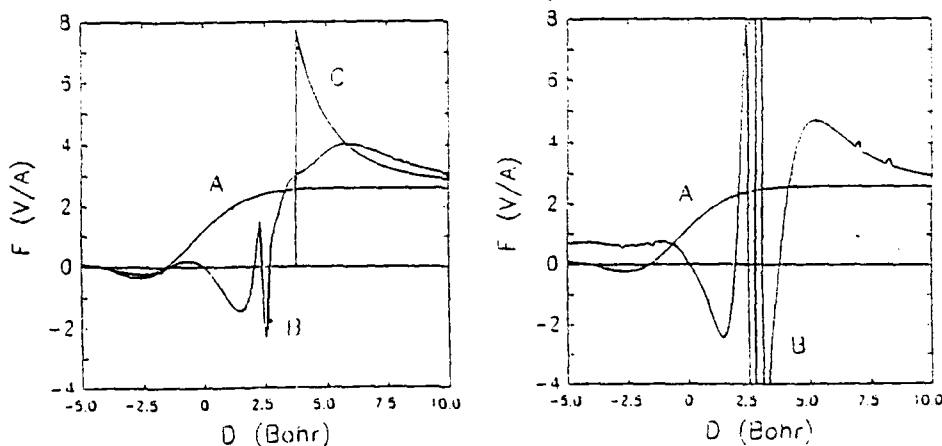


Fig. 3: Electrostatic field strength along line through the center of the adatom for Ti (left) and Rh (right) on a metal. Curves A and B: without and with the adatom; curve C: classical result.

well. In Fig.3 we plot, curve A, the external electric field laterally far from the lonely atom. Curve B is the field along a line through the center of the atom, and curve C is the classical result

approximating the atom by a hemispherical boss. Compared with the field in the absence of the adatom, we note the expulsion of the field from the adatom region, which results in an enhancement of the field just outside the adatom, however, not as much as classical theory predicts. Rather, the partial field penetration into the adatom region results in a smearing out of the field as a reflection of the adjustability of the electronic distribution at the surface. Evaporation field strengths, i.e. the fields at which metal atoms desorb at zero temperature, and dipole moments of the adatom have also been calculated in this model yielding good agreement with experimental values. In closing we note that the local field enhancements predicted in Fig.3, have recently been confirmed in precision measurements of field ion appearance energies.[10]

3. Field evaporation

Field evaporation is the removal of lattice atoms as singly or multiply charged positive ions from a metal in a strong electric field F of the order of several $V/\text{\AA}$, as it occurs at field ion tips [18,19]. The term field desorption is usually reserved for the process of removing field-adsorbed atoms or molecules from a field ion tip [11-12]. Field evaporation and field desorption are thermally activated processes; as such, their rate constants can be parameterized according to Frenkel-Arrhenius as

$$r_d = \alpha(T, F) \nu(T, F) e^{-Q(F)/k_B T} \quad (1)$$

Here $Q(F)$ is the field dependent height of the activation barrier to be overcome by the desorbing particle. The field and temperature dependent prefactor ω , contains a factor α accounting for the efficiency of the charge and energy transfer mechanism, and an effective "attempt" frequency ν to overcome the activation barrier. The minimum field strength beyond which at low temperatures the metal tip evaporates is termed the evaporation field strength; it varies from $2.5V/\text{\AA}$ for Ti to $6.1V/\text{\AA}$ for W with a typical experimental error margin of 10-15% [12]. Ernst has measured $Q(F)$ and $\nu(F)$ for Rh [13], and Kellogg [14] has presented data for W in the field range 4.7 to $5.9V/\text{\AA}$.

Two phenomenological models have been used in the past to calculate the activation energy $Q(F)$, the "image-force" model [15] and the "charge-exchange" model [16]. A recent assessment has been given by Kellogg [14]. Field evaporation is a dramatic demonstration of the limitation of classical concepts in solid state physics. Maxwell's theory says that the electric field drops to zero at the image plane, i.e. just outside the metal. Thus the electric field has, classically, no effect on the ion cores of the metal, and thus, classically field evaporation is not possible. On the other hand, we have seen in section 2 that field expulsion from the metal is not complete and that the field strength at the topmost ion cores in a

metal can be substantial, and in particular strong enough to cause field evaporation.

Experiment suggests that field evaporation of metal atoms occurs most likely at steps, kinks and edges or for small clusters of atoms on larger planes. Theory should calculate the electric field, the electron density, and the geometry of the ion cores for such configurations selfconsistently. In an early attempt Kreuzer and Nath [17] have used the ASED-MO cluster method taking the electric field again from jellium calculations, i.e. foregoing the selfconsistency requirement. Still, their calculation of evaporation field strengths reproduced trends in experimental data remarkably well. Selfconsistency was recently achieved within the context of density functional calculations for an adatom on a jell-

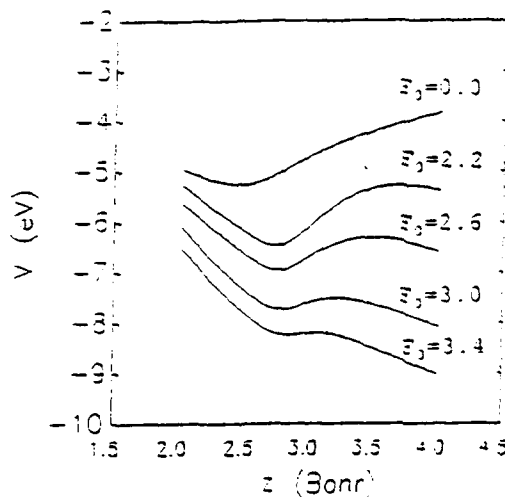


Fig.4: Potential energy for Nb on jellium with $r_s \approx 3.0$ bohr as a function of nuclear distance, z , from the jellium edge. F_0 in $V/\text{\AA}$.

lium surface.[8] In Fig.4, we show the adiabatic energy curves for niobium on jellium for several field strengths. In zero field the depth of the surface potential is 5.2eV, which is, not surprisingly, somewhat less than the cohesive energy of Nb, 7.47eV, because the jellium lacks p - and d -orbitals. This deficiency is also the cause of the rather weak repulsion at short distances. With a field applied, the ground state energy curves must assume an asymptotic form $-eF_0z$ for large z , appropriate for a singly charged positive ion. Ionization of the adatom can occur when its highest occupied level is lifted by the field energy term, eF_0z , above the Fermi level of the jellium. If the ionization level were not shifted and broadened by the interaction with the metal, the changeover to the asymptotic form would happen abruptly at the apex of the potential energy curve, i.e. at the point where the diabatic energy curves for the neutral and ionic species cross. For the fields chosen for Fig. 3, the apex is so close to the metal surface that considerable inter-

action between the adatom and the metal is still in effect. This results in a considerable broadening of the ionization level of the adatom so that only partial charge draining occurs in the apex region.

We will call the energy difference between the minimum of the surface potential and the local maximum at its apex the activation energy, $Q(F_0)$, for ionization. In zero field, the activation energy is equal to the binding energy of the adatom. We note that the activation energy becomes zero for the evaporation field strength which we estimate for Nb on jellium to be $3.6V/\text{\AA}$, which compares very favorably with the experimental value for Nb, $F_{ev}=3.5V/\text{\AA}$. Similar results are obtained for other metals.

It has been suggested [17] that the field dependence of the activation energy for different metals obeys a universal scaling law if one plots $Q(F_0)/Q(F_0=0)$ as a function of $f=F_0/F_{ev}$. In a simple model, this scaling law is given by

$$Q(F_0)/Q(F_0=0) = \sqrt{1-f} + \frac{1}{2}f \ln[(1-\sqrt{1-f})/(1+\sqrt{1-f})] \quad (2)$$

Experimental data on tungsten [14] and theoretical results obtained in the jellium model [8] and by the ASED-MO method [17] have confirmed this conjecture.

4. Field-induced Chemisorption

It has been known since the invention of the field ion microscope that the imaging gas, usually helium or neon, adsorbs on the tip in electric fields of the order of the best image field strength, i.e. several volts per angstroms, at standard operating temperatures around 80K [18-20]. In particular, field-adsorbed helium on a tungsten tip is bound by about 250meV in fields of the order of $4-5V/\text{\AA}$. Two mechanisms have been proposed to explain field adsorption: (i) polarization (dipole-dipole) forces [21-22] and (ii) field-induced chemisorption [23-24]. A consensus has emerged over the past few years that polarization forces are not sufficient to explain field adsorption of rare gases [25-26]. We will therefore skip this subject and proceed with a review of field-induced chemisorption.

As discussed earlier, electric fields of the order of volts per angstroms are comparable to those experienced by valence electrons in atoms and molecules. One should therefore expect that in external fields of that magnitude a redistribution of the valence electrons in the coupled adsorbate-solid system takes place which effects both the orbitals of the surface bond as well as internal bonds in an adsorbed molecule. Whether this redistribution leads to enhanced or reduced binding depends on whether bonding or antibonding orbitals are more strongly affected. We will refer to this phenomenon as field-induced chemisorption. Very surprisingly it is important even for the most inert atom, namely helium, i.e. in fields of the order of $5V/\text{\AA}$ polarization induces the occupation of

excited states at the level of a few percent. Thus even helium cannot, in such fields, be regarded as a closed shell atom with the consequence that it forms weak covalent bonds as it approaches a metal surface.

In our early work [23-24,27] on field-induced chemisorption of rare gases we have used the atom superposition and electron delocalization molecular orbital method (ASED-MO) [28]. The resulting field dependence of the activation energy, the position of the minimum in the adsorption potential and the vibrational frequency of

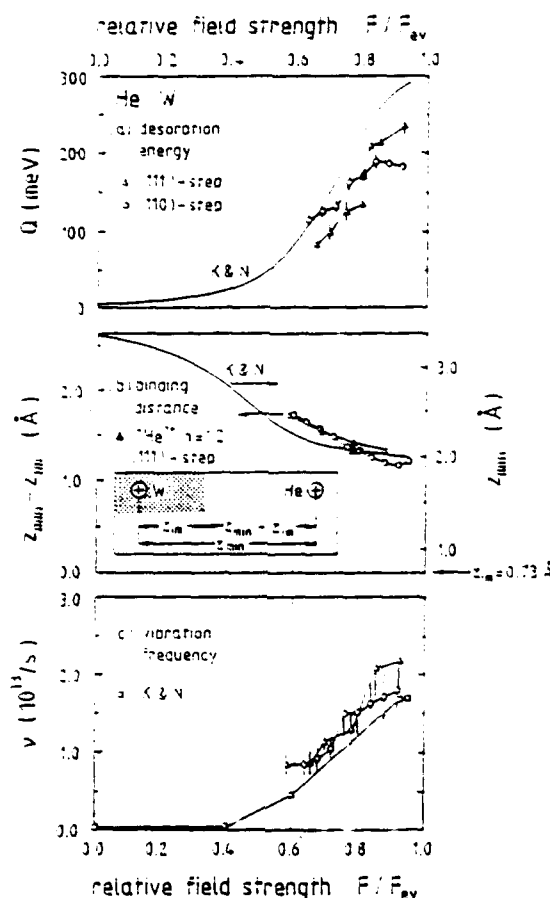


Fig.5: Activation energy Q , binding position z_{min} , and vibration frequency of helium field-adsorbed on tungsten.

the He atom in the surface potential is depicted in Fig.5 together with experimental results [27].

Exciting as these results may be one must be aware of a number of caveats with the ASED-MO method as discussed in Ref.29. We have therefore performed a selfconsistent calculation for the field-adsorption of helium and neon on a jellium surface using density functional theory in the local density approximation. Not only are the earlier results based on the semi-empirical ASED-MO theory reproduced, but new insight into the transition from physisorption

to covalent chemisorption is obtained; for details see Ref.29. it should be obvious that field effects are also important in understanding the manipulation of xenon atoms with a scanning probe.

5. Field-induced Chemical Reactions

To estimate the field strength needed to affect the chemistry of a reaction, we note that the equilibrium constant, K , of a reactive system depends on the field strength, F , via a van't Hoff equation [30]

$$\frac{\partial \ln K}{\partial F} = \frac{\Delta M}{RT} \quad (3)$$

where ΔM is a partial molar energy related to the change in electric moment in the reaction, i.e. $\Delta M = \Delta pF + \frac{1}{2}\Delta\alpha F^2 + \dots$. Here Δp is the difference in the permanent dipole moments of the products and the reactants, and $\Delta\alpha$ is the change in their polarizability. In order to achieve values for ΔM comparable with typical reaction enthalpies or volumes, one needs fields in excess of 0.1V/Å.

Block and coworkers, following earlier work by Inghram and Gomer [31] have developed a field pulse technique in the field ion microscope that allows the investigation of the field effect on chemical reactions; a detailed account has been given by Block.[32] Systems that have been studied by this technique are the formation of metal subcarbonyls, the polymerization of acetone, the reaction of sulphur on metal surfaces, the decomposition of methanol on metal surfaces, hydride formation on semiconductors, NO reactions on metals and many more.

As an example we will look, in this section, at the adsorption, dissociation and reaction of NO on a Pt(111) surface in high electric fields. Although NO adsorbed on various planes of platinum does not dissociate at room temperature, applying electric fields in excess of 0.4V/Å causes rapid decomposition. Employing pulsed field desorption mass spectrometry, Kruse *et al* [33] observed N_2O^+ , N_2^+ and, to a lesser extent, O^+ ions from the stepped Pt(111) regions of a field emitter tip as the field is increased, with decreasing amounts of NO^+ being recorded. Beyond 1.2V/Å no NO^+ could be desorbed.

In zero field NO adsorbs on Pt(111) [34] (and on Ni(111) [35] and on Ru(001) [36]) in bridge (on top) sites at low (high) coverage with an outward negative (positive) dipole moment. This flexibility is due to the lone electron in the 2π antibonding level, consisting mainly of the $2p_x$ levels of O and N. This picture has been confirmed by ASED-MO calculations which are also used to study the field effects.[37]

As an electric field is applied, the levels on the O atom, being further away from the surface, are raised up relatively higher than

those on the N atom. This in particular effects the $2p_x$ levels on O and N resulting in a shift of the electronic charge of the 2π level to the O atom. As a result the overlap between the 2π level of NO and the levels of the metal decreases with a subsequent decrease in the electron transfer from the metal to the 2π level stabilizing the adsorbed NO molecule. Also note that the dipole moment of adsorbed NO , i.e. O^-N^+ , is opposite to the field direction, thus the total energy increases as the field is increased.

Using the ASED-MO method [37] one can study the effect of an electric field on the bending mode of adsorbed NO . One finds that for fields larger than about 0.4 V/\AA the activation energy for dis-

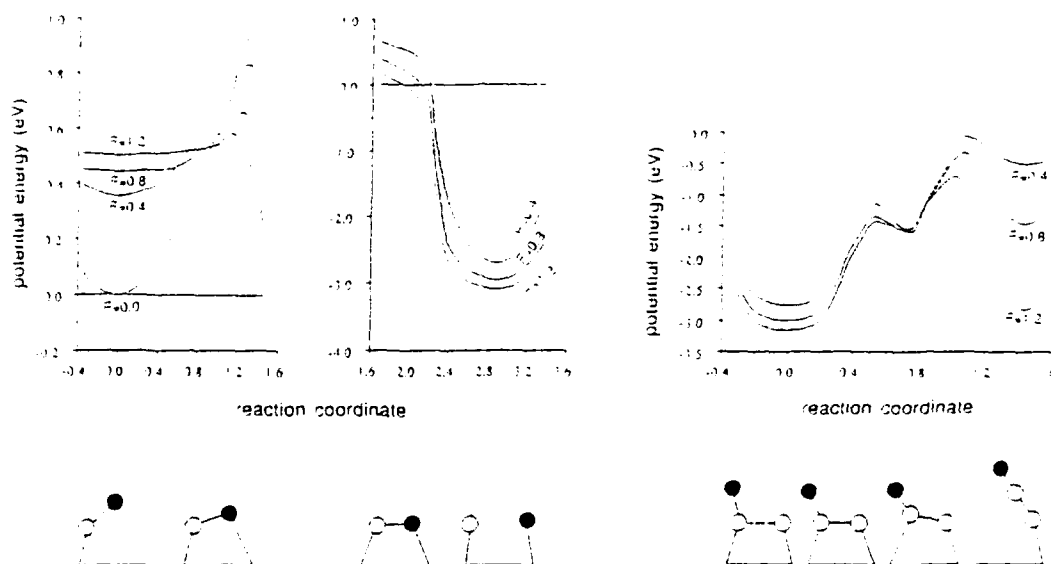


Fig.6: Potential energy curves and adsorption geometries of NO on $Pt(111)$ as a function of reaction coordinate.

sociation becomes negligible, see Fig.6. In fields larger than 1.2 V/\AA we finally observe the reaction $2NO \rightarrow N_2O + O$. A detailed discussion of the electronic structure of the species involved and the reaction pathways can be found in Ref.[37].

Outlook

Electric fields of the order of volts per angstrom affect the valence electrons on atoms shifting their energies by electron volts with respect to each other. In recent years a microscopic theory has emerged that looks at the new physics and chemistry from a microscopic point of view. We now understand field adsorption as field-induced chemisorption, a mechanism that affects even the lightest rare gases. We also now have a microscopic theory to describe kinetic effects in high electric fields at surfaces such as thermal field desorption and field evaporation [38-39].

The electronic structure calculations have been based so far on two vastly different approaches, namely the semi-empirical tight binding (ASED-MO) method and density functional theory. Where comparisons are possible, an astonishing degree of agreement in the predictions is found. The reason for this lies in the fact that fields of the order of volts per angstrom shift electronic levels in atoms and molecules by several eV relative to each other. Such large shifts can obviously be handled quite reliably by semi-empirical methods.

Chemistry in high electric fields is an even more exciting field. Because fields of the order of $V/\text{\AA}$ affect the valence electrons of atoms, new molecular species are stabilized in high fields thus opening up new reaction pathways in heterogeneous catalysis. Most work so far has been concentrating on static electric fields; however, many new phenomena are to be expected in alternating fields as well, as the work on photon-induced field desorption suggests.

What is important to learn from the example of field-induced chemistry in the last section is the fact that high electric fields can significantly alter reaction pathways, and indeed promote or hinder entire reactions. The fields involved are typically less than $1 V/\text{\AA}$, i.e. of the order of those generated between a tunneling tip and a substrate metal or semiconductor under conditions of atomic manipulation.

Acknowledgment

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